COMPARISON AND EVALUATION OF AGGLOMERATED MOFS IN GASEOUS BIOFUELS PURIFICATION BY MEANS OF PRESSURE SWING ADSORPTION (PSA)

José Antonio Delgado, Universidad Complutense of Madrid, Madrid, Spain
jadeldob@ucm.es
Vicente Ismael Águeda, Universidad Complutense of Madrid, Madrid, Spain
María de los Ángeles Uguina, Universidad Complutense of Madrid, Madrid, Spain
Pablo Brea, Universidad Complutense of Madrid, Madrid, Spain
Carlos A. Grande, SINTEF Materials and Chemistry, Oslo, Norway

Key Words: MOF, gaseous biofuels, purification, PSA

Metal-organic frameworks (MOFs) are crystalline structures consisting on metal ions coordinated to organic ligands. Porous MOFs are often formed with extremely high surface areas and other marvelous properties for adsorption processes. Although, to be used in industrial processes, MOFs should be agglomerated, being a key aspect because they properties usually are deteriorated compared with the powder [1]. Among industrial applications of adsorption, the recovery and purification of hydrogen from steam methane reforming (SMR) off-gases and the production of gaseous biofuels such as biomethane from biogas and biohydrogen have a great economic interest. Biomethane and biohydrogen could be recovered from mixtures containing carbon dioxide as main impurity by means of adsorption using pressure swing adsorption (PSA). The knowledge of the adsorption equilibrium and kinetics of the gaseous components in the targeted mixtures is the basis for the design of a PSA process for its separation.The aim of this work is the study of adsorption equilibrium and kinetics of H_2, N_2, CO, CH_4 and CO_2 on three different agglomerated MOF structures. The adsorbent performance on a typical PSA unit for hydrogen and methane purification has been evaluated by simulation.

Cu-BTC, ZIF-8 and UTSA-16 MOFs have been agglomerated using the procedure described before [1]. These materials have been characterized using scanning electron microscopy (SEM), Hg porosimetry and N_2 adsorption isotherm at 77K. The specific surface area of the agglomerated materials decreased less than a 5% compared with powder samples.H_2, N_2, CO, CH_4 and CO_2 high pressure equilibrium isotherms up to 50 bar at 298, 313 and 338 K have been measured and the results have been fitted using the Dual Langmuir model (table 1). Henry constants and diffusivities have been calculated using the chromatographic method described elsewhere [2].

Table 1. Dual Langmuir fitting parameters

Adsorbent	Gas	n_{max1}, mol kg^{-1}	n_{max2}, mol kg^{-1}	b_{01}, Pa^{-1}	b_{02}, Pa^{-1}	□□□H_1), kJ mol^{-1}	□□□H_2), kJ mol^{-1}
A-Cu-BTC	H_2	10.53	0	$4.91\cdot10^{-9}$	0	4.69	0
A-Cu-BTC	N_2	7.66	0	$1.16\cdot10^{-9}$	0	13.98	0
A-Cu-BTC	CH_4	6.31	3.59	$2.16\cdot10^{-10}$	$5.64\cdot10^{-9}$	20.27	12.34
A-Cu-BTC	CO	0.32	4.93	$1.23\cdot10^{-15}$	$3.84\cdot10^{-10}$	68.75	21.12
A-Cu-BTC	CO_2	7.37	4.64	$2.28\cdot10^{-10}$	$1.89\cdot10^{-10}$	24.49	24.97
A-ZIF-8	H_2	16.83	0	$7.49\cdot10^{-10}$	0	6.15	0
A-ZIF-8	N_2	5.09	0	$1.805\cdot10^{-9}$	0	11.35	0
A-ZIF-8	CH_4	5.84	0.99	$9.05\cdot10^{-10}$	$1.75\cdot10^{-9}$	15.15	13.36
A-ZIF-8	CO	34.17	0	$3.20\cdot10^{-10}$	0	11.22	0
A-ZIF-8	CO_2	10.76	1.34	$9.24\cdot10^{-11}$	$2.89\cdot10^{-9}$	22.27	13.74
A-UTSA-16	H_2	3.43	0	$2.04\cdot10^{-9}$		7.68	
A-UTSA-16	N_2	1.33	1.77	$2.15\cdot10^{-8}$	$1.67\cdot10^{-12}$	8.56	30.28
A-UTSA-16	CH_4	2.15	0.77	$1.52\cdot10^{-10}$	$7.18\cdot10^{-8}$	23.12	7.65
A-UTSA-16	CO	2.58	1.43	$6.96\cdot10^{-10}$	$7.13\cdot10^{-10}$	16.74	16.68
A-UTSA-16	CO_2	4.08	1.29	$6.00\cdot10^{-11}$	$1.63\cdot10^{-13}$	34.25	37.82

Finally, the physical adsorbent properties measured, the Dual Langmuir isotherm coefficients and kinetic parameters estimated and have been used in the design of a PSA unit. The cycle is simulated with a computer program in FORTRAN developed by Universidad Complutense of Madrid (PSASIM®).

[1] Carlos A. Grande, Vicente I. Águeda, Aud I. Spjelkavik, Richard Blom, Chem. Eng. Sci. 2015, 124, 154-158. DOI: 10.1016/j.ces.2014.06.048

[2] Vicente I. Águeda, José A. Delgado, María A. Uguina, Pablo Brea, Aud I. Spjelkavik, Richard Blom, Carlos A. Grande, Chem. Eng. Sci., 2015, 124, 159–169. DOI: 10.1016/j.ces.2014.08.039